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13. ABSTRACT (Maximum 200 words)
This final report describes research and development activities at the UTK Plasma Scientific Laboratory which were supported by the Army Research Office Contract DAAL-03-89-G-0104. Accomplishments during this four year period include building up an operational plasma ion implantation facility, the successful plasma ion implantation of aluminum and stainless steel with nitrogen ions, and the demonstration of significantly increased corrosiopn resistance and pitting potential in these metals. During the course of exploratory research activities, the regimes of ion energy, implantation voltage, and dose were identified which produced significantly improved corrosion resistance, and techniques for plasma ion implantation and corrosion resistance testing were perfected.

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Final Report on ARO Grant DAAL03-89-G-0125
For the Period October 1, 1989 to September 30, 1993

CORROSION INHIBITION BY PLASMA ION IMPLANTATION

Submitted to
The Army Research Office
Materials Science Division

by

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UTK Plasma Science Laboratory
Report No. PLS 95-2

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ABSTRACT

This final report describes research and development activities at the UTK Plasma Science Laboratory which were supported by the Army Research Office Contract DAAL 03-89-G-0105. Accomplishments during this four year period include building up an operational plasma ion implantation facility, the performance of corrosion-inhibition feasibility studies involving ion beam implantation of aluminum with nitrogen, titanium, silicon, chromium and tungsten ions, the successful plasma ion implantation of aluminum and stainless steel with nitrogen ions, and the demonstration of significantly increased corrosion resistance and pitting potential in these metals. During the course of exploratory research activities, the regimes of ion energy, implantation voltage, and dose were identified which produced significantly improved corrosion resistance, and techniques for plasma ion implantation and corrosion resistance testing were refined.

EXECUTIVE SUMMARY

Research Program Overview

This final report describes research and development activities at the UTK Plasma Science Laboratory which were supported by the Army Research Office contract DAAL-03-89-G-0105 at a level of $287,293 under Dr. Robert R. Reeber, ARO Program Manager, during the period from October 1, 1989 to September 30, 1993. The first three years of this four year period were supported by the ARO funds quoted above; the fourth year was a no-cost extension by ARO which was supported by the UTK Center for Materials Processing. This work is an outgrowth of the ARO Short Term Innovative Research Program contract DAAL-03-88-K-0161, funded at a level of $19,984, which spanned the period from July 1, 1988 to December 31, 1988, also entitled "Corrosion Inhibition by Plasma Ion Implantation". This work was also supported in part by the UTK Center for Materials Processing, which supported the research effort entirely during the 9 month gap between the Short Term Innovative Research program and the contract of which this is a final report; and it also supplied cost sharing during the first three years of DAAL-03-89-G-0125, the fourth year of the above contract, and our efforts since the termination of this contract on September 30, 1993.

During the four year period covered by this report, five archival scientific papers were published or submitted for publication, and thirteen oral or poster papers were presented at APS and IEEE meetings. During the four year period of ARO contract DAAL 03-89-G-0125, it supported two postdoctoral associates for a total of two person-years, two completed graduate theses, one graduate thesis which was completed during 1994, and a Ph.D. dissertation which will be completed in May, 1995, approximately seven person-years of half time GRA research and training, and the preparation of seven routine reports to the Army Research Office.

Also during the four year period of this contract, we have built up an operational plasma ion implantation facility which is now capable of routinely implanting nitrogen and other ions into metallic workpieces. This facility is one of perhaps five located at universities within the United States, and the only one in the southeastern United States. While the plasma ion implantation facility was being developed, we conducted corrosion inhibition feasibility studies using ion beam implantation in cooperation with the Oak Ridge National Laboratory. Since our plasma ion implantation facility became operational, we have developed and refined the techniques required to accomplish reliable and reproducible nitrogen plasma-ion-implantation at the doses and implantation energies required to yield significant improvements in the corrosion resistance of aluminum and stainless steels. Furthermore, we have developed reproducible and reliable techniques for the electrochemical assessment of changes and/or improvements in the pitting potential and corrosion resistance of aluminum and stainless steels, and we have published these results.

Objectives of Research

The objectives of our research program at the UTK Plasma Science Laboratory were to develop a facility for the reproducible and reliable plasma ion implantation of metals, to develop reproducible and reliable electrochemical methods for assessing the effects of plasma ion implantation on the corrosion resistance and pitting potential of metals, and then to determine the plasma and operating parameters that produced the largest possible increase in the pitting potential and corrosion resistance of such metals as aluminum and stainless steel when implanted with nitrogen and other ions. In particular, it was our objective to determine the ion dose, the implantation energy, and other operating parameters which led to the greatest improvements in the corrosion resistance of the metals under test.

Research Results

By far the greatest amount of our time and effort was required to build up a facility for the plasma ion implantation of metals. We have designed, built, and successfully operated the Microwave Plasma Facility (MPF), a 206 liter uniform plasma generated by 2.45 GHz microwave power. The uniformity of this plasma has applications outside the limited field of plasma ion implantation, and our presentation of this facility at professional society meetings has resulted in well over 100 reprint requests from industrial and university researchers. In addition to the Microwave Plasma Facility, we also built up a specialized switching circuit for the application of pulsed high voltage to the sample during the ion implantation process. Our switching circuit is based upon a tetrode vacuum tube, which can switch up to 2.8 amperes on and off against implantation voltages of up to 50 kV, with a current rise and fall time of less than 1 microsecond. The Microwave Plasma Facility and the associated switching circuit function reliably as a plasma ion implantation facility, and has been used to implant stainless steel and aluminum samples with nitrogen ions at energies up to 25 kV.

The implanted samples have been analyzed by electrochemical potentiodynamic methods, and we have repeatedly demonstrated improvements in the pitting potential of 304L stainless steel of up to a factor of 2 by plasma ion implantation of nitrogen. We also observe significant increases in the corrosion resistance of aluminum (1100A1) by plasma ion implantation of nitrogen. Feasibility studies by ion beam implantation at the Oak Ridge National Laboratory have also demonstrated significantly improved corrosion resistance of aluminum after implantation of either chromium or tungsten. One of our key findings with respect to the corrosion resistance of plasma ion implanted stainless steel is that the largest increases in pitting potential and corrosion resistance occur at ion doses and implantation voltages considerably below those which are optimum for improvements in hardness and

wear. For example, in 304L stainless steel, the optimum implantation voltage for corrosion resistance is between 10 and 20 kV, and the optimum dose appears to be approximately 10^{15} ions per square centimeter. These numbers contrast with voltages of 50 kV and above, and doses of 10^{17} and above, which are optimum for significant improvements in hardness and wear.

Utility of Results to the Army

Our results so far indicate that aluminum alloys (commercially pure 1100 and 2014) can have their corrosion resistance enhanced by implantation of chromium, tungsten or nitrogen, and that stainless steel (304L) can have its pitting potential and corrosion resistance significantly increased by plasma ion implantation at relatively low implantation voltages and doses. For the stainless steel, the low voltages and doses are easier to achieve than those required for significant improvements in hardness and wear resistance. Although we have not done so, it may be possible to demonstrate improvements in corrosion resistance, hardness, and wear by a two-step implantation process, one involving low voltages and doses for the improvement of corrosion resistance, and a second treatment involving higher voltages and doses for the improvement of hardness and wear resistance.

The utility of plasma ion implantation for the permanent improvement of corrosion resistance of Army equipment in the field must rely on the integrity of the ion-implanted surface layers on the material. The doses and energies which produce improved corrosion resistance correspond to penetrations of no more than a few hundred atomic layers. This thin, protective layer of ion implanted metal, although probably harder and more abrasion resistant than the unimplanted metal, may nevertheless be subject to abrasive damage which could result in the loss of corrosion resistance. Thus, the abrasion resistance of the

corrosion-resistant ion implanted surface layer is a critical consideration with regard to practical utility.

RESEARCH OBJECTIVES

The objectives of this research program from its inception on July 1, 1988 as an ARO Short Term Innovation Research Program until the present, have been four fold: First, to design, build and debug the specialized apparatus needed for plasma ion implantation; second, to perfect the methods and apparatus needed to successfully plasma ion implant common metals of interest to the Army and US industry with nitrogen and other ions likely to produce significant improvements in corrosion resistance; third, to screen the very large number of possible combinations of implanted ions, energies, doses, and workpiece materials by collaborative research using ion beam implantation at the Oak Ridge National Laboratory; and fourth, to develop the apparatus and methods to test plasma ion implanted samples for improvements in pitting potential and corrosion resistance.

Apparatus for Plasma Ion Implantation

At the inception of this research effort with the ARO Short Term Innovative Research Program grant on July 1, 1988, there existed only one plasma ion implantation apparatus in the country, that of Conrad at the University of Wisconsin. We recognized from the beginning that it would be necessary to build a facility capable of plasma ion implanting samples of significant size and volume. Neither the high voltage switching circuits nor the large volume uniform plasmas required for plasma ion implantation were available off-the-shelf. Our first task was to build a high voltage switching circuit capable of switching up to 50 kV on a sample immersed in a plasma, and preferably to do so with current and voltage rise and cut-off times on the order of a microsecond or less, over pulse

durations on the order of tens of microseconds, and with a variable repetition rate between pulses.

It soon became obvious that in addition to a flexible high voltage switching circuit,we needed a large volume, steady state, uniform, unmagnetized plasma in which to expose the workpieces and samples to the plasma ion implantation process. The Penning discharge on which we performed our first implantations was magnetized up to 0.2 tesla, and this led to significant differences in the dose and corrosion resistance characteristics, depending on whether the sample was oriented parallel to or normal to the magnetic field lines. When the ARO contract DAAL 03-89-G-0125 was funded, we immediately began the design and fabrication of the Microwave Plasma Facility, a photograph of which is shown in Fig. 1. This facility consisted of a stainless steel vacuum tank, fabricated in the shops of the UTK Department of Materials Science and Engineering, which was approximately one meter high and 50 centimeters in diameter. We also developed a 2.4 GHz microwave power supply and feed system which was capable of supplying up to 2 kw of power to a plasma generated in this vacuum tank. The resulting 206 liter plasma was measured by Langmuir probing, and found to be both radially and axially quite uniform, an important requirement for the plasma ion implantation of irregular or large objects. The number density of this plasma was in the mid 10^{16} per cubic meter range, thus it is therefore capable of supplying large fluxes of ions to the sample during plasma ion implantation.

Plasma Ion Implantation of Samples

The second major objective of our research program was to develop the methods, plasma operating conditions, and hardware necessary to reliably produce plasma ion implantation of samples in the Microwave Plasma Facility. In doing this, it is necessary to make the best possible quantitative measurements of the total current and current density

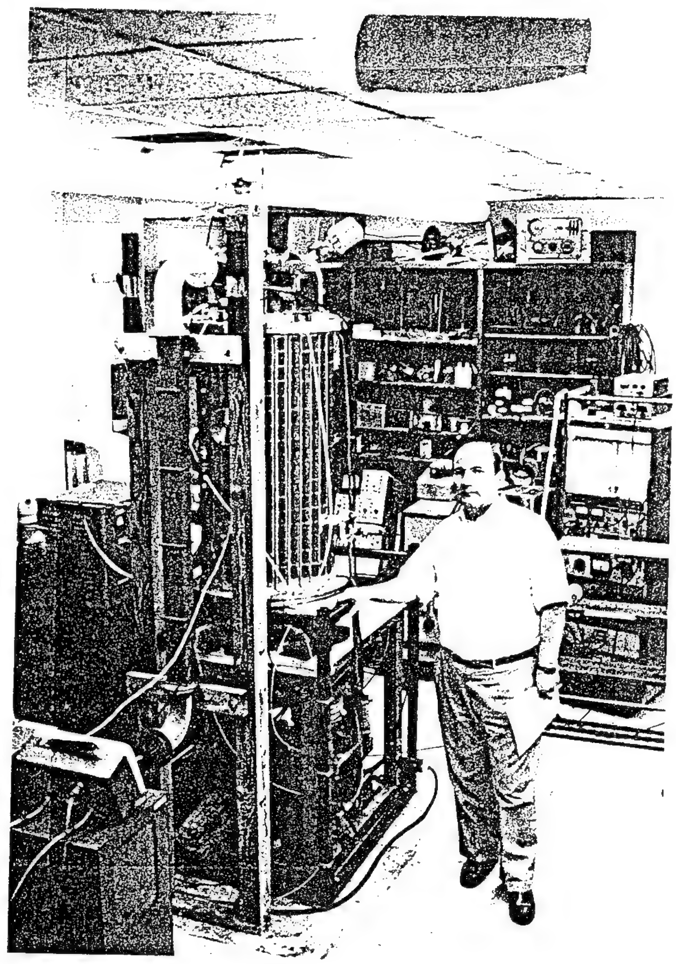

Figure 1. Photograph of the Microwave Plasma Facility (MPF) in May, 1991 in the configuration to be used for plasma ion implantation.

flowing to the sample during plasma ion implantation, and also to make sure that the implantation process occurs uniformly over the surface of the workpiece. This objective is nontrivial, since the use of square or rectangular workpieces or samples produced noticeable nonuniformities at the edges and at the diagonals of square samples, which were observed, for example, by the color change of the surface under high implantation doses.

Testing of Samples

Once the implantation apparatus and methodology are available, it then becomes necessary to develop methods for the electrochemical evaluations of parameters related to corrosion resistance. The sample preparation methods and potentiodynamic operating methods were standardized for application to aluminum or stainless steel samples, and produced reliable baseline data for unimplanted samples. The proper preparation of samples and the generation of anodic polarization curves (potential vs. anodic current density) produced reliable data on the degree of corrosion resistance in a chloride environment, including the change in the pitting potential (vertical shift of the knee on the polarization curve). The anodic polarization curves were found to be sensitive to the method of sample preparation before implantation, and also to the methods used to prepare the sample for the polarization run after implantation.

RESEARCH RESULTS

In this section we summarize the results of our research program citing, where appropriate, the location of additional information in the Appendices of this report or in the publications listed in Table I, copies of which are on file with the ARO.

Table I

Publications on Plasma Ion Implantation

Supported by ARO

Archival Papers and Conference Proceedings:

1. Williams, J. M., Gonzales, A., Quintana, J., Lee, I.-S., Buchanan, R. A., Burns, F. C., Culberson, R. J., Levy, M., and Treglio, J. R.: Ion Implantation for Corrosion Inhibition of Aluminum Alloys in Saline Media. Nuclear Instruments and Methods in Physics Research B59/60, 1991, pp. 845-850.

2. Spence, P. D.; Keebler, P. F.; Freeland, M. S. and Roth, J. R.: A Large-Volume, Uniform, Unmagnetized Microwave Plasma Facility (MPF) for Industrial Plasma Processing Applications. Invited Paper, 10th International Symposium on Plasma Chemistry, Workshop on Industrial Plasma Applications and Engineering Problems, August 10, 1991, Bochum, Germany (1991).

3. Kamath, S. G.; Roth, J. R.; Smith, P. P.; and Buchanan, R. A.: A Large-Volume, Nonresonant Microwave Plasma Facility (MPF) for Plasma Ion Implantation. Proc. 1st International Workshop on Plasma-Based Ion Implantation, Madison, WI, August 4-6, 1993.

4. Smith, P. P.; Buchanan, R. A.; Kamath, S. G.; and Roth, J. R.: Enhanced Pitting Corrosion Resistance of 304L Stainless Steel by Plasma Ion Implantation. Proc. 1st International Workshop on Plasma-Based Ion Implantation, Madison, WI, August 4-6, 1993. (Also published in Journal of Vacuum Science and Technology.)

5. Roth, J. R.; Kamath, S. G., Liu, C.; Buchanan, R. A.; and Smith, P. P: An Empirically Based Model for the Sheath Characteristics on a Sample Undergoing Plasma Ion Implantation. 1st International Workshop on Plasma-Based Ion Implantation, Madison, WI, August 4-6, 1993.

Oral and Poster Conference Presentations

1. Roth, J. R.: Theory of Plasma Ion Implantation for Hardening Metals. 1987 IEEE International Conference on Plasma Science, June 1-3, 1987, Arlington, VA, IEEE Catalog #87CH2451-3 (1987) pp. 123-124.

2. Keebler, P. F.; Crowley, J. E.; and Roth, J. R.: A High-Voltage Switching Circuit for Rapid Plasma Ion Implantation. 1989 IEEE International Conference on Plasma Science, May 22-24, 1989, Buffalo, NY, IEEE Catalog No. 89CH2760-7 (1989) p. 149.

3. Roth, J. R.; Keebler, P. F.; Buchanan, R. A.; and Lee, I.-S.: Corrosion Inhibition by Plasma Ion Implantation. Proc. Joint Workshop Research and Technology Transfer-Ion Implantation Technology for Specialty Materials, Knoxville, TN October 26-27, 1989 ARO WRKSP-R91-01, February, 1991.

4. Crowley, J. E.; Keebler, P. F.; and Roth, J. R.: A High-Voltage Switching Circuit for Rapid Plasma Ion Implantation. APS Bulletin, Vol. 34 (1989) p. 2021.

5. Keebler, P. F. and Roth, J. R.: A Microwave Generated Plasma for Ion Implantation Studies. 1990 IEEE International Conference on Plasma Science, May 21-23, 1990, Oakland, CA, IEEE Catalog # 90CH2857-1 (1990) p. 161.

7. Keebler, P. F., Freeland, M. S. and Roth, J. R.: A Large-Volume, Unmagnetized, Microwave Generated Plasma for Industrial Plasma Engineering Applications. APS Bulletin, Vol. 35 (1990) p. 2016.

8. Spence, P. D.; Freeland, M. S.; and Roth, J. R.: Performance of a Large-Volume, Unmagnetized Microwave Plasma Facility (MPF) for Plasma Ion ImplantationApplications. APS Bulletin, Vol. 36 (1991) p. 2385.

9. Kamath, S. and Roth, J. R.: Observations of the Sheath Thickness on a Sample Undergoing Plasma Ion Implantation. APS Bulletin, Vol. 37 (1992), p. 1452.

10. Yu, S.; Kamath, S.; and Roth, J. R.: Stabilization of the Microwave Plasma Facility (MPF) by a Microwave Isolator. 1993 IEEE International Conference on Plasma Science, June 7-9, 1993, Vancouver, B.C., IEEE Catalog No. 93 CH3334-0 (1993), p. 213.

11. Kamath, S.; Yu, S.; and Roth, J. R.: Observation of Sheath Characteristics on a Sample Undergoing Plasma Ion Implantation. 1993 IEEE International Conference on Plasma Science, June 7-9, 1993, Vancouver, B. C., IEEE Catalog No. 93 CH3334-0 (1993), p. 101.

13. Kamath, S. G.; Liu, C.; and Roth, J. R.: A Model for the Sheath Surrounding Objects Undergoing Plasma Ion Implantation. APS Bulletin Vol. 38 (1993) p. 1900.

14. Roth, J. R.; Kamath, S. G.; Liu, C.; Buchanan, R. A.; and Smith, P. P.: Plasma Ion Implantation Research at the University of Tennessee, Knoxville. Proc. 1st International Workshop on Plasma-Based Ion Implantation, Madison, WI August 4-6 1993 (1993).

Masters Theses at UTK

1. Keebler, Philip F.: A Large-Volume Microwave Plasma Facility for Plasma Ion Implantation Studies. Masters Thesis in the UTK Department of Electrical and Computer Engineering, August 1990.

2. Gupta, Abhijit: Corrosion Inhibition Through Nitrogen Implantation into Aluminum by Ion Beam and Plasma Source Ion Implantation. Masters Thesis in the UTK Department of Materials Science and Engineering, December, 1991.

3. Kamath, Sanjay G.: Factors Affecting the Plasma Ion Implantation of Metallic Samples. Masters Thesis in the UTK Department of Electrical and Computer Engineering, May, 1994.

Ph.D. Theses at UTK

1. Smith, Preston Paul: Ion Implantation Applications for Pitting Corrosion Inhibition-(Tungsten Beam Implantation of Aluminum and Nitrogen Plasma Ion Implantation of 304L Stainless Steel). Ph.D. Dissertation, University of Tennessee, Knoxville, May 1995.

Switching Circuit

The high voltage switching circuit developed during the Short Term Innovative Research Program grant from ARO during 1988 is described in detail in the master's thesis of Mr. Philip F. Keebler, a copy of which has been submitted to ARO. The electrical characteristics of the switching circuit also were presented at two professional society meetings in 1989 which are listed as Items 2 and 4 in the oral and poster presentations in Table 1.

The switching circuit developed for our research was designed and tested for negative DC potentials up to 50 kV, and during an implantation pulse could deliver currents up to 2.8 amperes under nominal plasma conditions.

Implantation in a Penning Discharge Plasma

Upon completion of the high voltage switching circuit in late 1988, the only plasma available in which to perform plasma ion implantation was a Penning discharge plasma

which had been used previously for a basic research contract with the Office of Naval Research. This plasma provided number densities up to 10^{16} electrons per cubic meter at electron temperatures of typically 5 to 8 electron volts, in a cylindrical plasma column about 12 centimeters in diameter, and in a magnetic field that was 0.2 tesla.

Although we were able to run several anodic polarization curves for the implantation of nitrogen into stainless steel which indicated significant increases in the pitting potential of the stainless steel, the data were not reliable due to the anisotropy imposed by the magnetic field. For this reason, we concluded after only a few experimental runs in the Penning discharge that it was both desirable and necessary to develop an entirely different plasma specifically intended for plasma ion implantation applications. It was evident from the Penning discharge data that such a plasma should be unmagnetized, to avoid the anisotropy occasioned by the magnetic field direction, and should be uniform and of large volume, in order to allow the implantation of large samples, as well as to minimize the interactions of the workpiece during implantation with the walls of the vacuum vessel.

Development of the Microwave Plasma Facility

Based on our previous experience with the Penning discharge, we decided to design a plasma facility specifically for plasma ion implantation. We wanted several hundred liters of plasma uniform over the entire volume, and at number densities from 10^{15} to 10^{16} electrons per cubic meter. We used computer aided design methods to design the Microwave Plasma Facility (MPF) which is shown in Figure 1. The details of the mechanical design of this facility, its service ports, and its auxiliary equipment are detailed in the master's thesis of Philip F. Keebler, A copy of which is on file with the ARO. The design and mechanical characteristics of the MPF are described in entries 5 through 7 of the oral and poster conference presentations listed in Table 1.

By mid-1991, the Microwave Plasma Facility was ready for use as a plasma ion implantation facility, and we then moved the switching circuit and other accessories needed for plasma ion implantation from the Penning discharge to the Microwave Plasma Facility. In the period from July 1991 to the end of 1992, we continued to make refinements in the microwave circuitry and components, including the installation of a reflected power isolator, as well as a four-stub tuning section of a new design. Documentation of the plasma-related behavior of the Microwave Plasma Facility with the isolator and new tuning stub was reported in entry #11 among the oral and poster conference presentations listed in Table 1, and also in the proceedings of the Madison Workshop on Plasma Related Ion Implantation, which is listed as #3 of the archival paper and conference proceedings listed in Table 1.

Corrosion Inhibition Studies

Before presenting a summary of the major results obtained on corrosion inhibition by plasma ion implantation (PII), the authors wish to acknowledge the extremely valuable cooperation and contributions of J. M. Williams, Solid State Division, Oak Ridge National Laboratory (ORNL). During the development of the PII capability at the University of Tennessee, Knoxville (UTK), when PII corrosion studies per se were not possible, corrosion feasibility studies were performed in cooperation with Mr. Williams using the more traditional ion-beam implantation (IBI) method. Early studies also were performed in cooperation with researchers at the Corpus Cristi Army Depot, Corpus Christi, TX and the U. S. Army Materials Technology Laboratory, Watertown, MA. At a later stage in the project, when the UTK PII source became operational for implantation of nitrogen, the interactions with Mr. Williams at ORNL continued in terms of comparing PII and IBI corrosion results and defining doses and dose distributions by Rutherford backscattering spectroscopy (RBS). At a still later stage in the project, when interest developed regarding

the possible beneficial corrosion effects associated with implanting tungsten into aluminum, Mr. Williams' cooperation made this study possible using the IBI method. At present, no PII system, regardless of location, has been developed to the capability of implanting metallic species. However, with regard to major break-throughs in corrosion inhibition, we believe the PII method must be advanced to this capability. Therefore, the IBI work on tungsten in aluminum is regarded as preliminary to future PII studies.

The major corrosion results obtained in the project are summarized in the following sections.

Ion Beam Implantation of N, Ti, Si and Cr into 1100 Aluminum and 2014 Aluminum Alloy. N, Ti, Si and Cr were individually implanted into 1100 aluminum and/or 2014 aluminum alloy at various doses and energies at ORNL using the IBI process. Relative to corrosion characterization, electrochemical potentials corresponding to pit initiation and pit propagation in 1 wt. % NaCl solution were determined at UTK. Further corrosion characterizations were performed by exposing the 2014 Al samples to 168-hour salt-fog tests at the Corpus Christi Army Depot; the results are shown in Figure 2. It is apparent that Cr implantation is very effective in minimizing the aqueous corrosion of 2014 Al in NaCl environments. The details of this study are fully described in the paper, "Ion Implantation for Corrosion Inhibition of Aluminum Alloys in Saline Media," J. M. Williams, A. Gonzales, J. Quintana, I.-S. Lee, R. A. Buchanan, F. C. Burns, R. J. Culbertson, M. Levy and J. R. Treglio, Nuclear Instruments and Methods in Physics Research B59/60 (1991), 845-850 (Item #1 in the archival papers and conference proceedings of Table I).

Ion Beam Implantation and Plasma Ion Implantation of N into 1100 Aluminum. Nitrogen was implanted into aluminum at 20 KeV and with doses at and near 10^{17} ions/cm^2 by IBI at ORNL and by PII at UTK. The effects on pit initiation and pit

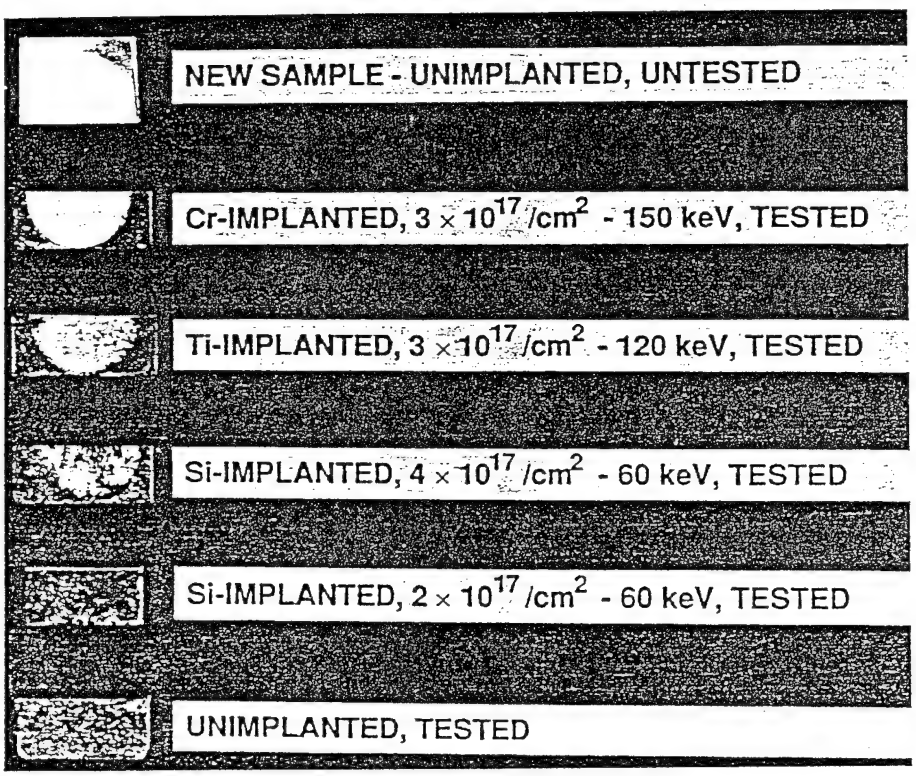

Fig. 2. Photograph showing coupons of 2014 Al, new, after various ion implantation treatments and salt fog testing, and as-tested with no ion implantation. Starting surfaces were all mechanically polished. Ion implanted areas were 2 cm in diameter, and the ion implanted samples were halved after salt testing. 168 h salt fog test.

propagation were determined by measuring pitting potentials and potentials corresponding to an anodic current density of 1 mA/cm^2, respectively, in deaerated 1 wt. % NaCl solution. The nitrogen implantation was found to have no beneficial effect on pit initiation; the pitting potential was not changed. However, there was a significant reduction in pit propagation rate due to nitrogen implantation by both the IBI and PII processes. To confirm this effect, anodic current densities at a constant potential greater than the pitting potential were measured as a function of time for unimplanted and implanted samples. An example of these results is shown in Figure 3, where it is seen that in the deaerated solution, the current density is significantly less for the nitrogen implanted aluminum. The details of this study are fully described in the M. S. thesis, "Corrosion Inhibition through Ion Beam and Plasma Source Ion Implantation," Abhijit Gupta, M. S. Thesis, University of Tennessee, Knoxville, December, 1991, a coy of which is on file with the ARO.

Plasma Ion Implantation of N into 304L Stainless Steel. Because of the known beneficial effects of nitrogen additions by normal melt/solidification processes on the pitting resistance of austenitic stainless steels, it was decided to evaluate the effects of nitrogen ion implantation by the PII process on the pitting resistance of 304L stainless steel. It is noted that other major effects, in addition to chemistry modification, accompany the ion implantation process, e.g., defect formation, residual stress development, etc. These additional effects could compromise the chemistry-modification effect. Nitrogen was implanted into 304L stainless steel at 10 and 20 KeV and over a dose range from 10^{14} to 10^{18} ions/cm^2. Under the conditions of these experiments, the implanted nitrogen was found to significantly improve the pitting resistance of 304L in 1 wt. % NaCl solution, but only over a dose range near 10^{15} ions/cm^2, with the optimum effect being at the lower implantation energy, 10 KeV. The dose effect is illustrated in Figure 4, where the maximum pitting potential is seen to occur near 10^{15} ions/cm^2. The cause for this effect is

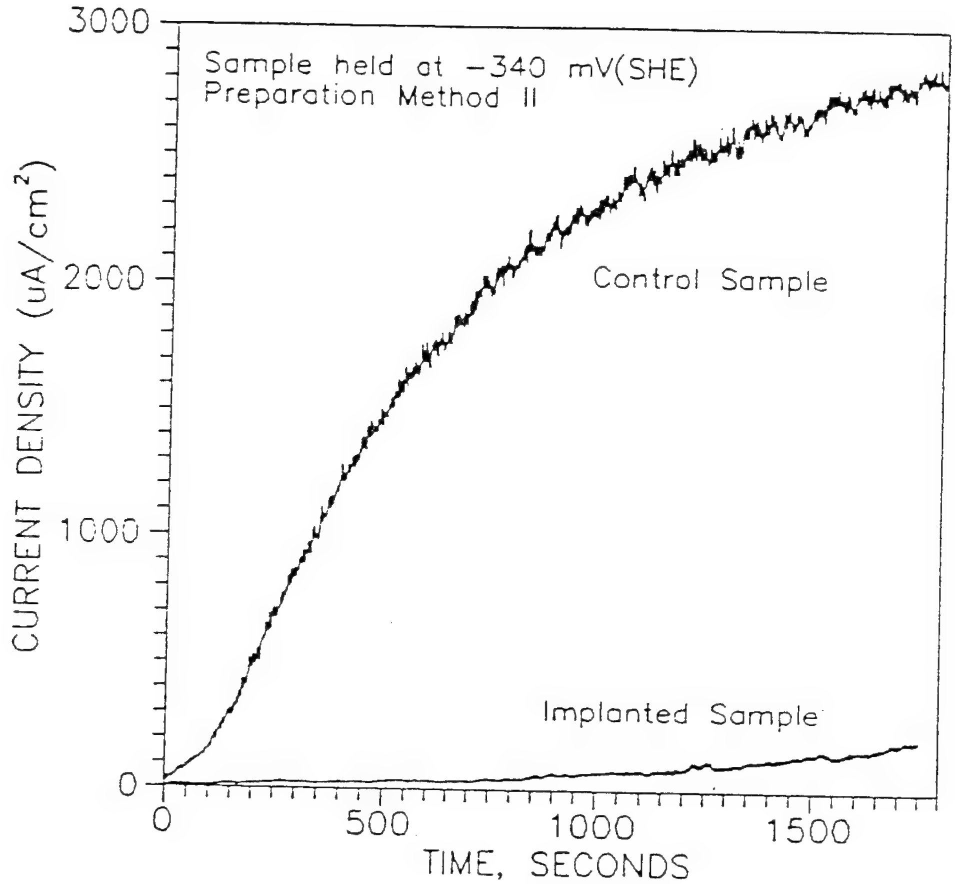

Fig. 3. Anodic current density versus time at -340 mV(SHE) for 1100 Al unimplanted (control) and nitrogen implanted at 20 KeV, 3×10^{17} atoms/cm^2.

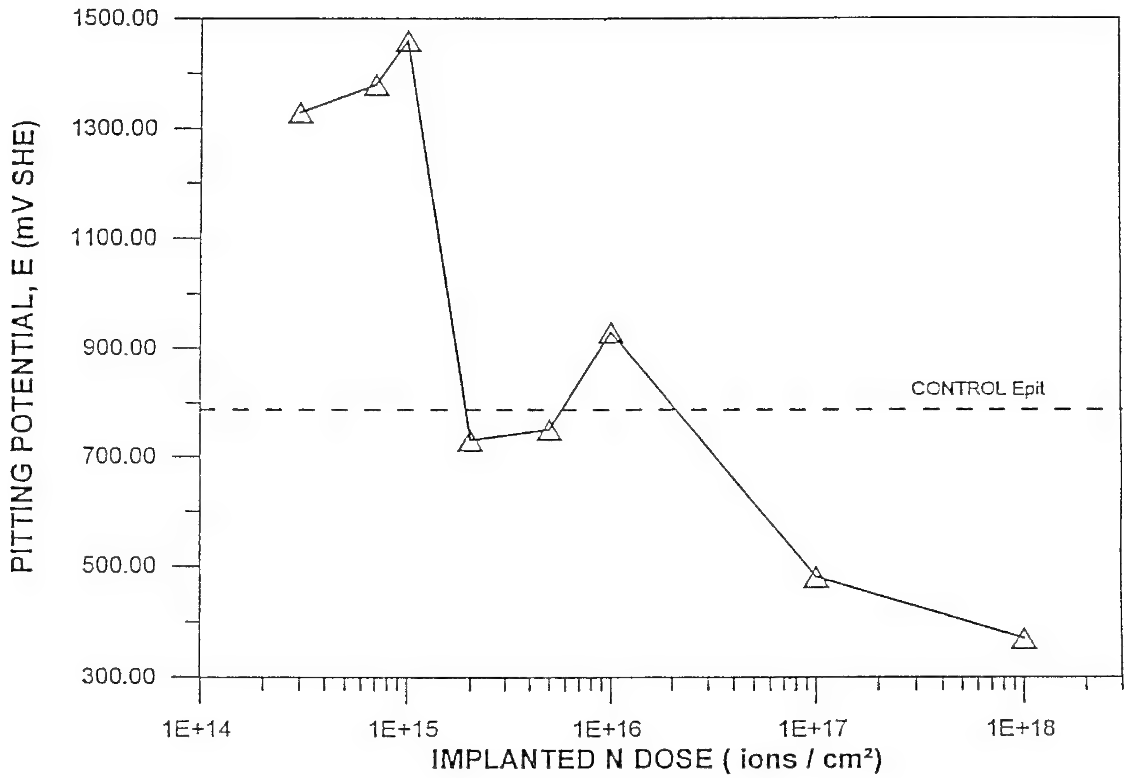

Fig. 4. Effect of nitrogen-ion-implantation dose at 10 KeV on the pitting potential of 304L stainless steel in deaerated 1 wt. % NaCl.

postulated to be that below $\approx 10^{15}$ ions/cm^2, insufficient solid-solution nitrogen is present, and above $\approx 10^{15}$ ions/cm^2, local chromium depletion occurs due to chromium-nitride precipitation. The details of this study are fully described in the paper, "Enhanced Pitting Corrosion Resistance of 304L Stainless Steel by Plasma Ion Implantation," P. P. Smith, R. A. Buchanan, J. R. Roth and S. G. Kamath, accepted for publication (Sept., 1993) in Journal of Vacuum Science and Technology (Item #4 in the archival papers and conference proceedings of Table I).

Ion Beam Implantation of W into 1100 Aluminum. Current interest in the effects of tungsten ion-implanted into aluminum was stimulated by the work of Shaw, et al. (J. Electrochem. Soc., Vol. 138, No. 11, 1991) who evaluated the chloride-solution pitting potential of non-equilibrium thin-film alloys produced by co-sputtering Al with either Mo, W, Ta or Cr. W was found to be, by far, the most effective, with 9 at. % W increasing the pitting potential by as much as 2600 mV. In order to determine if the same outstanding results could be achieved by ion implantation, arrangements were made with J. M. Williams at ORNL to ion-beam implant W into commercially-pure 1100 aluminum at an energy of 60 KeV and over a dose range of 6×10^{15} to 9×10^{16} ions/cm^2 (corresponding to peak-maximum concentrations of approximately 2 to 28 at. % W at a depth of approximately 30 nm).

Corrosion evaluations were accomplished by performing anodic polarization tests in deaerated (N purged) 1.0 wt. % NaCl solution and evaluating the resultant pitting potentials. Samples in the lower W dose range produced little improvement in pitting potential, while samples in the higher dose range produced consistently good results, i.e., increases in pitting potential, but of varying magnitude. The best results, which have not yet been duplicated, are shown in Figure 5. For this W-implanted Al sample (5×10^{16} ions/cm^2) in the deaerated solution, the pitting potential was +1700 mV(SHE), whereas for

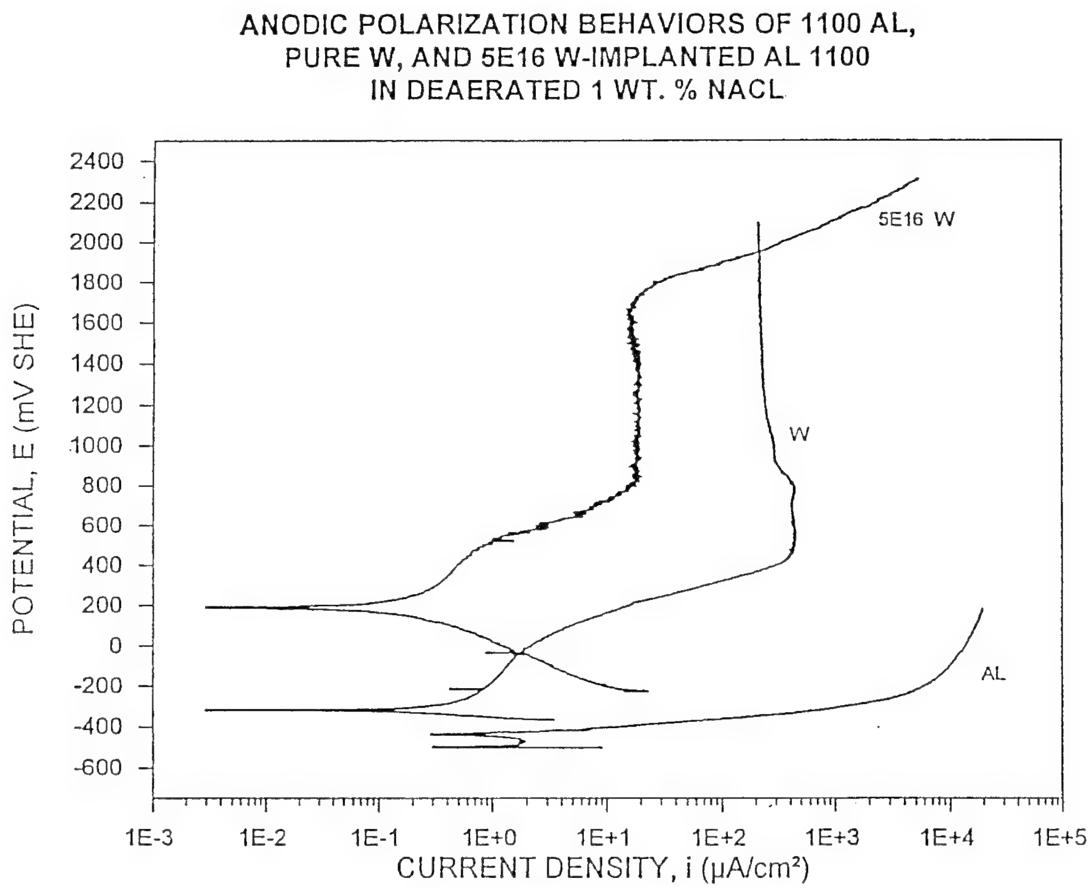

Fig. 5. Anodic polarization behaviors of 1100 aluminum, pure tungsten, and tungsten-implanted (60 KeV, 5 x 10^{16} ions/cm^2) 1100 aluminum in deaerated 1 wt. % NaCl.

the unimplanted Al, it was -450 mV(SHE) -- a difference of 2150 mV. However, such a dramatic increase in pitting potential was not generally observed. The more typical, and reproducible, results are illustrated in Figure 6, which in the deaerated solution reflects an increase in pitting potential of approximately 200 mV at W doses on the order of 5 x 10^{16} ions/cm^2. Although the 200 mV increase in pitting potential is not as dramatic as the 2150 mV increase, it is nevertheless significant.

To further evaluate the beneficial effects of W implantation, anodic polarization tests also were performed in the 1.0 wt. % NaCl solution under aerated (air sparged) conditions. Results are shown in Figure 7, where it is seen that the W implantation at doses of 3 x 10^{16} and 9 x 10^{16} ions/cm^2 still consistently produce increases in pitting potential on the order of 125 mV relative to that of the unimplanted Al.

Parameter Ranges for Optimum Effect

Our most studied system thus far is nitrogen implanted into 304L stainless steel. For this combination, we find that the pitting potential is increased by a factor of 2 for low doses (doses in the range of 10^{14} to 10^{15} ions per square centimeter), and that as the dose increases above about 10^{15} per square centimeter, the pitting potential drops to the control value. At the high doses required for significant changes in hardness or wear improvement, the pitting potential is at or below the unimplanted sample characteristics. There is also limited evidence at this time that the lower implantation voltages of 10 to 15 kV result in higher pitting potentials than nitrogen ions implanted at higher voltages of 20 kilovolts or more. Some of the evidence for this is discussed in paper #4 listed in Table 1. These observations may be understood in terms of the corrosion resistance being determined by the properties of the metal very close to the surface. Thus, while hardness and wear may require a significant depth or surface-layer thickness, the region that initiates and controls corrosion is confined to the uppermost atomic layers on the surface, and is

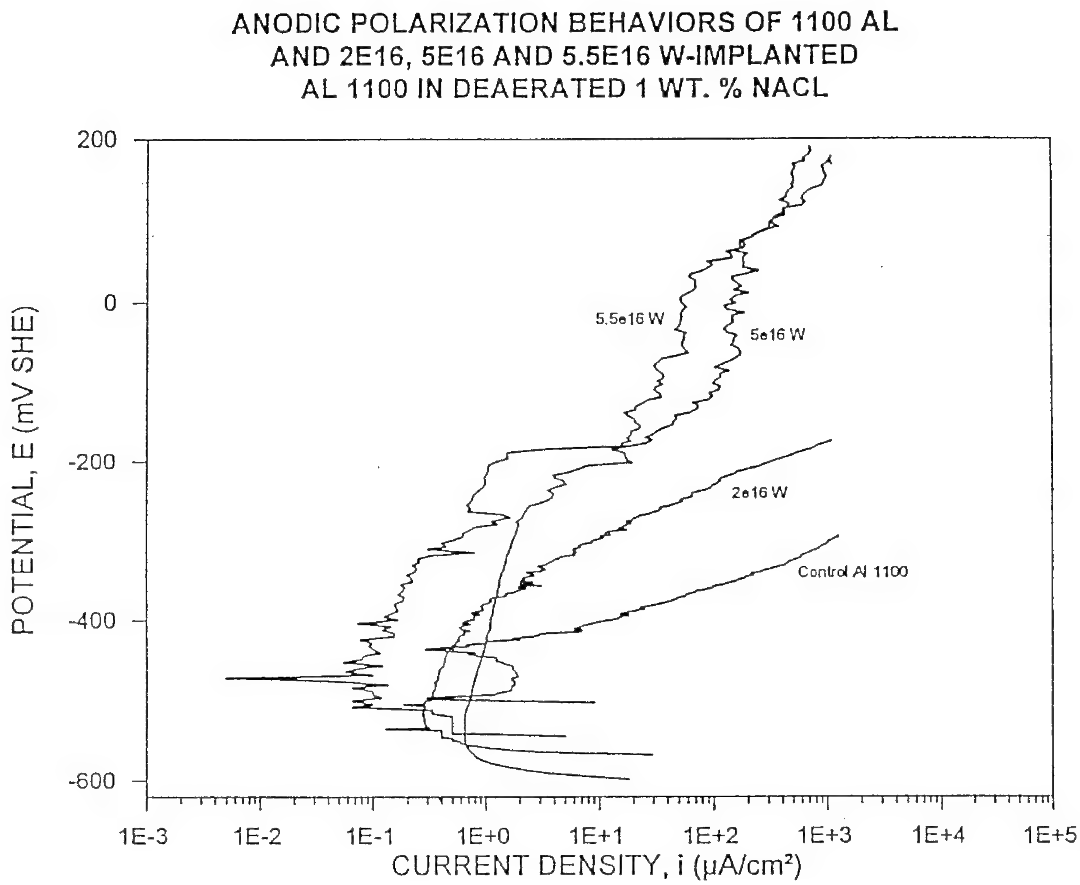

Fig. 6. Anodic polarization behaviors of 1100 aluminum and tungsten-implanted (60 KeV; 2 x 10^{16}, 5 x 10^{16} and 5.5 x 10^{16} ions/cm^2) 1100 aluminum in deaerated 1 wt. % NaCl.

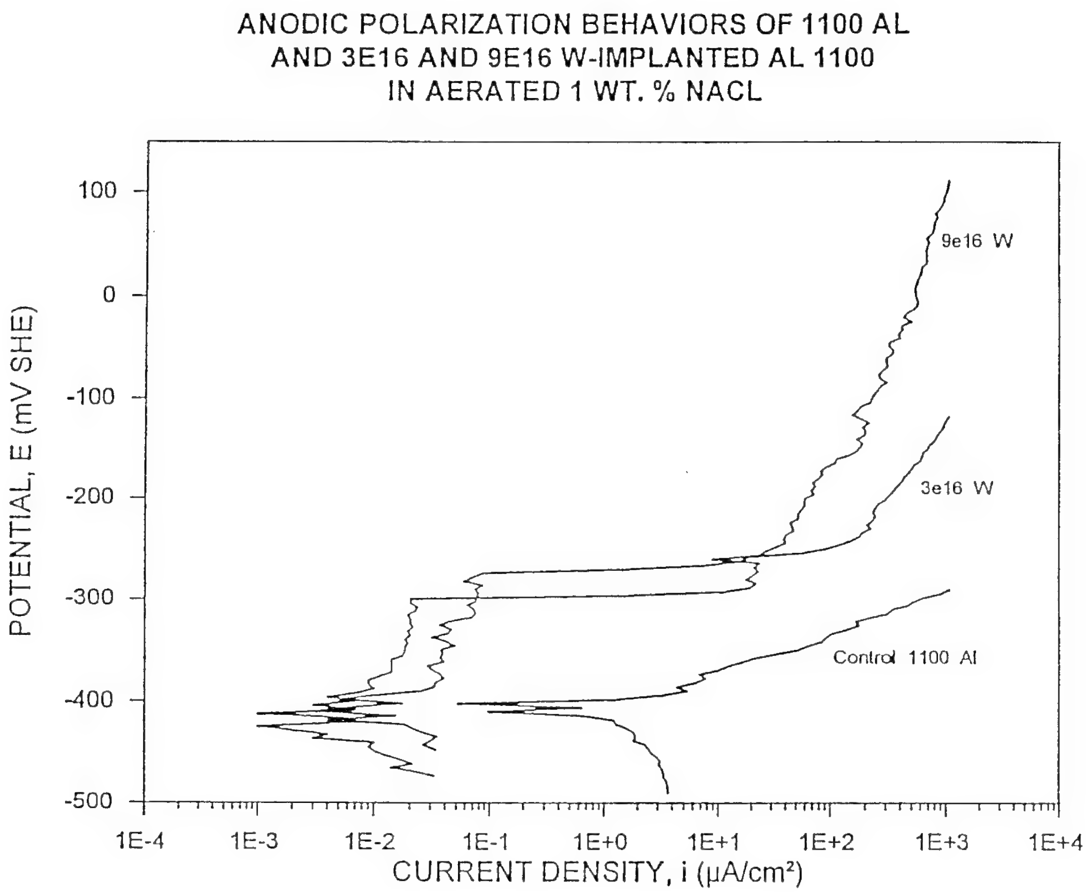

Fig. 7. Anodic polarization behaviors of 1100 aluminum and tungsten-implanted (60 KeV; 3 x 10^{16} and 9 x 10^{16} ions/cm^2) 1100 aluminum in aerated 1 wt. % NaCl.

effected by lower doses and lower energies which tend to deposit the ions near the surface. It thus appears that a single plasma ion implantation operation will not be adequate to improve both the corrosion related properties and the hardness or wear characteristics. However, it should be a relatively simple matter to program a plasma ion implantation operation to deposit the ions in a two step process, one depositing a relatively low dose of low energy ions to improve the corrosion resistance, followed by a high dose, high energy implantation to improve the hardness and wear characteristics.

PUBLICATIONS AND TECHNOLOGY TRANSFER

Archival Publications

This four year research contract has resulted thus far in five archival conference manuscripts, publications, or conference proceedings. These are full length reports of completed work. Two of these have been published in the literature, and three others have been submitted to the Journal of Vacuum Science and Technology as part of the proceedings of the Wisconsin workshop on plasma related ion implantation. These preprints and reprints are listed in Table 1.

Non Archival Conference Presentations

It is our custom at the UTK Plasma Science Laboratory to report semi-annually on the progress of our major research programs at the APS and IEEE plasma meetings. This opportunity to present poster papers on our work, whether progress reports or completed work, is a good opportunity for our postdoctoral students and senior graduate students to acquire experience in organizing, presenting, and defending their work before their professional peers. During the four year history of this research program, we presented fourteen such non-archival conference presentations, which are listed in Table 1.

Other Industrial and University Interactions

Two of the most intense interactions of our group with the plasma ion implantation community occurred during the ARO-sponsored workshops which we and our graduate students attended. The ARO-UTK Workshop on Research and Technical Transfer of Ion Implantation Technology for Specialty Metals was held in Knoxville on October 5 through 7, 1989. The program of that Workshop is included as Appendix H of this report. The proceedings of that workshop were published in 1991 by the Army Research Office. In addition, the Wisconsin Workshop on Plasma-based ion implantation, held on August 4 through 6, 1993, provided an appropriate occasion to summarize the research findings of this contract, and our group at UTK therefore submitted three full length papers to that conference.

In addition to the two ARO sponsored workshops on plasma ion implantation, the non-archival progress reports which we presented at the APS and IEEE plasma meetings also provided an opportunity to interact with the professional community, both those involved with plasma ion implantation, and a broader community of those from industry who were interested in, for example, our Microwave Plasma Facility and its large volume uniform plasma. At these APS and IEEE plasma meetings, we had probably 200 reprint requests for our papers on the Microwave Plasma Facility.

After the Wisconsin workshop in August of 1993, we were contacted by Mr. Robert J. Sinko of the Eastman Chemical Company, who was interested in the plasma ion implantation of punches used to make spinnerets for polymer fiber production. We exposed a number of punches for them at various dose levels in late August, but we have not yet heard back as to the results. We have hesitated until very recently to interact with industry, because, in the area of corrosion resistance at least, we did not feel that we had a

proper understanding of all the physical processes involved in both implantation and corrosion resistance, enough to justify involving industry.

International Collaboration

As part of a linkage agreement between the UTK Plasma Science Laboratory and the University of Electronic Science and Technology of China in Chengdu, P.R.C., the UESTC provided the UTK Plasma Science Laboratory with a microwave isolator and tuning network which allowed us to stabilize and greatly improve the tuning of the Microwave Plasma Facility. This equipment, worth several thousands of dollars, was donated to our research program at UTK, and was installed by Prof. Shanfu Yu from the University of Electronic Science and Technology of China, who worked at the UTK Plasma Science Laboratory for a six month period starting in September, 1992.

PARTICIPATING SCIENTIFIC PERSONNEL

The scientific personnel participating in this contract research over its four year history are listed in Table 2. Professors Roth and Buchanan served as Principal Investigator and Co-Principal Investigator, respectively, during the entire duration of the research program. We had two post-doctoral associates affiliated with the contract and paid by the research program as listed in Table 2. The total duration of their services was approximately 2 person-years. We had seven person-years of GRA effort, five individuals that were supported during the four year duration of the research.

During the four year duration of the contract, two students received their master's degrees, Mr. Philip F. Keebler who received his Master's degree in Electrical Engineering in August of 1990, and Mr. Abhijit Gupta, who received his Master's degree in Materials Science and Engineering in December of 1991. Mr. Preston Smith, who was supported by the contract from August 1, 1991 until the end of the research program on September 30,

1993, is to receive his Ph.D. in May, 1995, so this contract has supported Mr. Smith during much of his graduate program. In addition, Mr. Sanjay Kamath, who was supported by the contract from January 1, 1992 until the end of the contract on September 30, 1993, received his Master's degree in Electrical Engineering in May 1994, so that he, has had most of his graduate education supported by this contract research.

Table II

Participating Scientific Personnel

<u>Principal Investigators (Duration of Contract)</u>

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<u>Postdoctoral Associates</u>

In-Seop Lee (Inception until November 30, 1990)
Paul D. Spence (November 1, 1990 until June 30, 1991)

<u>Graduate Research Assistants</u>

1. Philip F. Keebler (inception until Aug. 31, 1990) Received M. S. in E. E. August, 1990.

2. M. Scott Freeland (August 1, 1990 until December, 1991).

3. Abhijit Gupta (January 1, 1991 until August 15, 1991). Received M.S. in M.S.&E. December, 1991.

4. Preston Smith (August 1, 1991 until September 30, 1993). To receive his Ph.D. in M.S. & E in May, 1995.

5. Sanjay G. Kamath (January 1, 1992 until September 30, 1993). Received his M. S. in E.E. May, 1994.

REPORT OF INVENTIONS

No patents were disclosed during the course of this research program. However, the development of the Microwave Plasma Facility represented an innovation that attracted widespread interest at plasma meetings, and resulted in about 200 reprint requests. The Microwave Plasma Facility is potentially useful for many applications of plasmas to the surface treatment of materials, as well as for microelectronic deposition and etching.